Structure of the Trimethylaluminum Dimer As Determined by Powder Neutron Diffraction at Low Temperature

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The structure of $Al_2(CD_3)_6$ has been determined at 4.5 K by powder neutron diffraction. The molecule crystallizes in space group $C2/c$. Salient bond distances and angles are as follows: $r(Al-C_b) = 2.145(7)/2.146(8)$ Å, $r(Al-C_t) = 1.945(6)/1.926(5)$ Å, $r(Al\cdots Al) = 2.700(10)$ Å, $r(C-D) = 1.061(4)-1.118(5)$ Å; $\angle C_b-Al-C_b = 102.0(3)°$, $\angle C_t-Al-C_t = 125.8(3)°$, $\angle C_b-Al-C_t = 108.8(4)°$, $\angle D-C-D = 99.0(4)-111.6(5)°$. The bridging CD_3 groups adopt a staggered conformation with respect to each other in a molecule with C_{2h} symmetry, and there is no evidence in the structure for the involvement of the C−D bonds in $Al-CD_3-Al$ bridge bonding. Variable-temperature studies show the lattice constant b to exhibit unusual behavior, initially decreasing with increasing temperature. This phenomenon is interpreted in terms of increasing thermal motion of the molecule with increasing temperature.

Introduction

Despite having been known since 1866,[1] trimethylaluminum ($AlMe_3$) still poses intriguing structural questions. While an equilibrium between monomeric and dimeric forms has been established in the gas phase, the dimer appears to be the sole species occurring in condensed phases. Within the realm of metal alkyl compounds, Al_2Me_6 is a rare example of a molecule possessing both terminal and bridging methyl groups.

An early X-ray diffraction study by Lewis and Rundle confirmed the methyl-bridged nature of Al_2Me_6.[2] Subsequently, the geometry of the heavy-atom skeleton was determined by a series of single-crystal X-ray diffraction studies below room temperature[3−5] and by a gas-phase electron-diffraction study.[6] The X-ray studies differed in their the description of the bridging $Al(\mu_2\text{-}CH_3)_2Al$ units. Vranka and Amma[3] and Nyburg et al.[4] interpreted their results in terms of a structure close to **I** (Chart 1), with significant distortion of the bridging methyl group from local C_{3v} symmetry and participation of a $C-H\cdots Al$ component in the bridging bond, a conclusion challenged by Cotton.[7] A subsequent study by Huffmann and Streib[5] favored structure **II(b)**, with pentacoordinated carbon atoms and no involvement of the C−H moieties in the bridge bonding, a conclusion which has also been supported by a ^{27}Al nuclear quadrupole resonance study.[8] The gas-phase electron-diffraction study[6] was not able to locate the hydrogen atoms with sufficient accuracy to discriminate between **I** and **II**.

Despite the high level of interest in the problem some 3 decades ago, the nature of the bridge bonding in Al_2Me_6 remains to be settled unambiguously. Recent quantum chemical calculations have shown molecular structure **II(a)**, with eclipsed bridging CH_3 groups and C_s symmetry, to be the most stable[9−11] but to lie only 0.3 kcal mol^{-1} lower in energy than the corresponding isomer **II(b)**, with these methyl groups in a staggered conformation and overall C_{2h} symmetry.[11] Remarkably, imposition of an alternative C_{2h} geometry on the dimer by rotating the bridging methyl groups to bring one C−H bond in each proximal to the Al atom and encourage $C-H\cdots Al$ bonding was found to raise the energy of the molecule by 20 kcal mol^{-1}.[11]

In view of the discrepancies outlined above and the importance of $AlMe_3$ and its derivatives in many catalytic and technological processes,[12] we have determined

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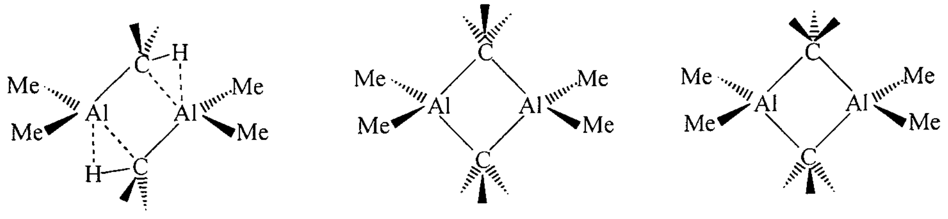
Chart 1



I **II(a)** **II(b)**

the structure of the trimethylaluminum dimer at very low temperature (4.5 K) by analysis of the neutron diffraction pattern produced by a microcrystalline sample of $Al_2(CD_3)_6$. The central importance of Al_2Me_6 to an understanding of metal−alkyl bonding in general, and in particular to the involvement of C−H bonds as ligands in organometallic chemistry and catalysis,[13] makes such a decisive structural determination timely and necessary. The scattering interaction between neutrons and the nucleus is essentially independent of the atomic number Z; hence, by studying the fully deuterated molecule we have located precisely the positions of all hydrogen nuclei and shown the molecule to conform to structure **II(b)**.

Experimental Section

Synthesis and Characterization. *Caution! Me_2Hg is extremely toxic and should be handled only under appropriate containment by experienced workers.* All operations were conducted in vacuo or under an Ar atmosphere using standard Schlenk and high-vacuum-line techniques and employing anhydrous materials.[14] $Al_2(CD_3)_6$ was prepared by the reaction of $(CD_3)_2Hg$, with Al powder (Aldrich), in an adaptation of a literature procedure.[15] $(CD_3)_2Hg$ was itself prepared by reaction of CD_3MgBr (Aldrich) with HgI_2 (Aldrich). The product was purified by fractional condensation in vacuo, and its purity was assessed by reference to the IR spectrum of the vapor.[16]

Neutron Diffraction Measurements. Numerous attempts to prepare a microcrystalline sample of $Al_2(CD_3)_6$ by rapid freezing of a liquid sample resulted invariably in preferred orientation within the solid. Ultimately, a satisfactory sample was prepared by controlled sublimation in vacuo of $Al_2(CD_3)_6$ vapor (ca. 1.5 g) into a standard 11 mm diameter vanadium can mounted on the end of a cryostat center stick. Neutron scattering patterns from this sample were recorded using the high-resolution powder diffractometer HRPD at the ISIS pulsed-neutron source of the Rutherford Appleton Laboratory. Data were recorded using a vanadium-tailed helium-flow "orange" cryostat over time-of-flight ranges of 30−130 and 110−210 ms, corresponding to a total d-spacing range of 0.6−4.2 Å at backscattering ($\langle 2\theta \rangle = 168°$). Lower angle (90 and 30°) detector banks enabled d spacings of, in this case, up to some 6.0 Å to be recorded—albeit at lower resolution—for the purposes of unit cell indexing and space group verification. Data were initially recorded at 4.5 K for a period of some 130 μA h ($3^{1}/_{2}$ h), during which time the sample was rotated about the vertical axis in order to minimize effects attributable to any residual preferred orientation in the powder. Subsequently, a set of shorter (15 μA h) measurements were made at a series of temperatures between 10 and 180 K.

Structure Refinements. The structure at 4.5 K was refined using the Rietveld method[17] implemented by the program TF12LS.[18] Atomic coordinates for the starting model were those given by Vranka and Amma;[3] however, bond length and bond angle constraints were required initially on refinement of the deuterium positions. No constraints were imposed during the final stages of refinement, and anisotropic displacement parameters were refined for all deuterium atoms.

Results and Discussion

Sections of the observed and calculated profiles for the 4.5 K refinement are shown in Figure 1, and the final calculated intra- and intermolecular bond lengths and angles for $Al_2(CD_3)_6$ are given in Tables 1 and 2, respectively. In agreement with the earlier X-ray diffraction experiments, Al_2Me_6 is found to crystallize in the centrosymmetric monoclinic space group $C2/c$. There is one $AlMe_3$ molecule in the asymmetric unit, the dimer being generated via a center of inversion at (0, 0, $^{1}/_{2}$). The positions of all hydrogen nuclei in Al_2Me_6 are thus determined accurately for the first time, and the molecule is shown to adopt in the crystal the structure shown in Figure 2, with symmetrical disposition of the bridging CH_3 groups between the two Al centers and C_{2h} molecular symmetry overall: there is no deviation from normality apparent either in the C−H bond distances or in the H−C−H angles within these groups which could be interpreted in terms of participation of the H atoms in the bridge bonding. The bridging CH_3 moieties adopt a staggered disposition with respect to each other (**II(b)**), rather than the computed lowest

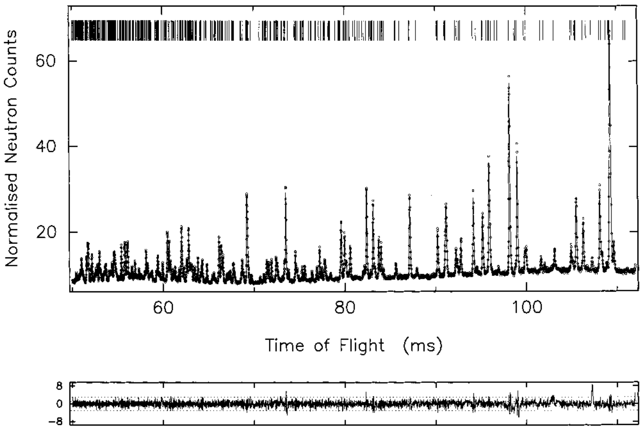


Figure 1. (top) Observed (dots) and calculated (line) and (bottom) difference profiles of the powder neutron diffraction pattern of Al_2Me_6-d_{18} at 4.5 K. Vertical tick marks represent the calculated peak positions.

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Table 1. Intramolecular Bond Lengths (Å) and Bond Angles (deg) for Al_2Me_6-d_{18} at 4.5 K[a]

bond distances		bond angles	
	Bridging		
Al−C(1)	2.145(7)	C(3)−Al−C(2)	125.8(3)
Al−C(1)′	2.146(8)	C(2)−Al−C(1)′	108.8(4)
	Terminal		
Al−C(2)	1.945(6)	C(1)′−Al−C(3)	105.3(3)
Al−C(3)	1.926(5)	C(1)−Al−C(1)′	102.0(3)
Al−Al′	2.700(10)	C(3)−Al−C(1)	109.3(3)
		C(2)−Al−C(1)	103.3(3)
	Bridge C−D		
C(1)−D(11)	1.103(3)	D(11)−C(1)−D(12)	107.0(3)
C(1)−D(12)	1.088(3)	D(11)−C(1)−D(13)	99.0(4)
C(1)−D(13)	1.097(4)	D(12)−C(1)−D(13)	106.3(3)
		D(21)−C(2)−D(22)	111.6(5)
	Terminal C−D		
C(2)−D(21)	1.061(4)	D(21)−C(2)−D(23)	106.2(4)
C(2)−D(22)	1.086(5)	D(22)−C(2)−D(23)	109.3(4)
C(2)−D(23)	1.118(5)	D(31)−C(3)−D(32)	105.4(4)
C(3)−D(31)	1.102(5)	D(31)−C(3)−D(33)	108.2(4)
C(3)−D(32)	1.097(5)	D(32)−C(3)−D(33)	107.5(4)
C(3)−D(33)	1.065(6)	Al−C1−Al′	78.0(3)
		Al′−Al−C(2)	116.0(3)
		Al′−Al−C(3)	118.1(3)

[a] The prime (′) denotes atoms transformed by the center of symmetry at the molecular center at (0, 0, $^1/_2$).

Table 2. Summary of Shortest Intermolecular Contacts (Å) for Al_2Me_6-d_{18} at 4.5 K

atoms	contact dist	no. of contacts	sym relation
D(23)···D(23)	2.279(7)	3	$-x, y, {}^1/_2 - z$
D(22)···D(21)	2.373(5)	2	${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$
D(23)···D(11)	2.498(5)	2	$-{}^1/_2 + x, -{}^1/_2 - y, -{}^1/_2 + z$
D(32)···D(12)	2.484(5)	3	$x, {}^1/_2 + y, z$

energy structure (**II(a)**) in which they are eclipsed. As only a single conformer is found in the crystal, the energy difference between these two conformers—calculated at 0.3 kcal mol^{-1} [11] and comparable to the electronic noise level in such calculations—is clearly insignificant compared to crystal-packing energies.

Table 3 collates the main skeletal dimensions determined for the Al_2Me_6 molecule from X-ray and neutron diffraction of the crystalline solid, from electron diffraction by the vapor, and by DFT calculations. Given the range of temperatures at which the different experiments were performed, and the intrinsic differences in the parameters deduced, there is generally good agreement on all but one dimension. This is the distance *r*(Al···Al), which is found by the neutron diffraction study to be ca. 0.1 Å longer than in all other cases. This feature is also reflected in the wider Al−C_b−Al angle deduced from the neutron diffraction data. A degree of Al···Al bonding certainly exists within the Al_2Me_2 bridged unit and may render this dimension somewhat flexible thermally, but since the neutron diffraction experiment was performed at the *lowest* temperature of any listed in Table 3, such metal−metal bonding is unlikely to explain satisfactorily this observation. The discrepancy may be due, in part, to the effects of libration within the structure at the elevated temperatures at which the X-ray measurements were made. Corrections for the effective foreshortening of bond lengths were not applied and can easily amount to 0.025 Å.[19] A more intriguing possibility may be the occurrence of dimer−dimer interactions at low temperatures (q.v.).

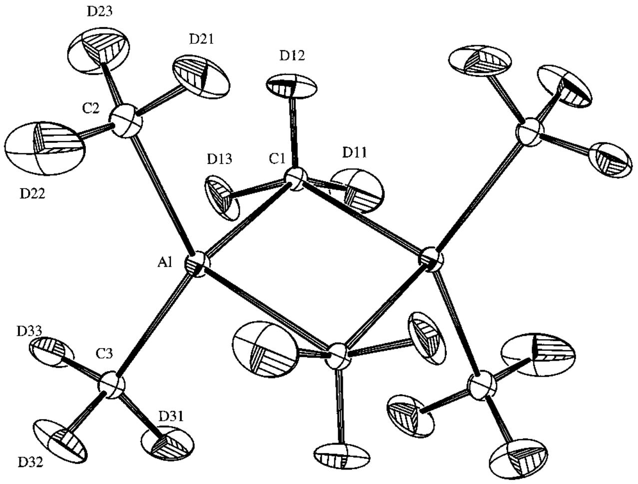

Figure 2. ORTEP plot[22] representing the final refinement of the structure of Al_2Me_6-d_{18} at 4.5 K. Thermal ellipsoids are drawn at the 50% probability level.

The unit cell parameters determined at a series of temperatures are shown in parts a−e of Figure 3, and selected unit cell parameters from the diffraction experiments performed on the crystalline solid are listed in Table 4. The tabulated data highlight large apparent systematic differences between the present neutron measurements and the earlier results from single-crystal X-ray studies which are well in excess of differences normally attributable to H/D isotope effects. The dimensions *a* and *c* increase as expected with increasing temperature, while the monoclinic angle *β* remains more or less invariant. In contrast, *b* decreases with increasing temperature, passing through a minimum at ca. 105

Table 3. Main Skeletal Dimensions of Al_2Me_6 As Determined by Experiment and by Computation

technique	temp/K	*r*(Al−C_b)/Å	*r*(Al−C_t)/Å	*r*(Al···Al)/Å	∠Al−C_b−Al/deg	∠C_t−Al−C_t/deg	ref
X-ray	103	2.125(2)	1.956(2)	2.606(2)	75.7(1)	123.2(1)	5
X-ray	223	2.134(10) 2.153(12)	1.983(10) 1.958(11)	2.600(4)	74.7(4)	123.1(4)	3
GED	333	2.140(4)	1.957(3)	2.619(5)	75.5(0.1)	117.3(15)	6
DFT		2.17	1.98	2.62	74.2		11
neutron	4.5	2.145(7)	1.945(7)	2.700(8)	78.0(3)	125.8(3)	this work

Table 4. Selected Unit Cell Parameters of Al_2Me_6 As Determined by Experiment

technique	temp/K	*a*/Å	*b*/Å	*c*/Å	*β*/deg	ref
neutron	4.5	12.0243(10)	6.9631(1)	14.0180(1)	122.300(1)	this work
neutron	105	12.2748(17)	6.8752(16)	14.2402(14)	122.699(5)	this work
X-ray	103	12.433(6)	6.919(2)	14.422(6)	123.21(1)	5
neutron	180	12.4162(17)	6.9024(2)	14.4133(15)	123.195(5)	this work
X-ray	223	12.74(2)	6.96(1)	14.63(2)	123.67(25)	3

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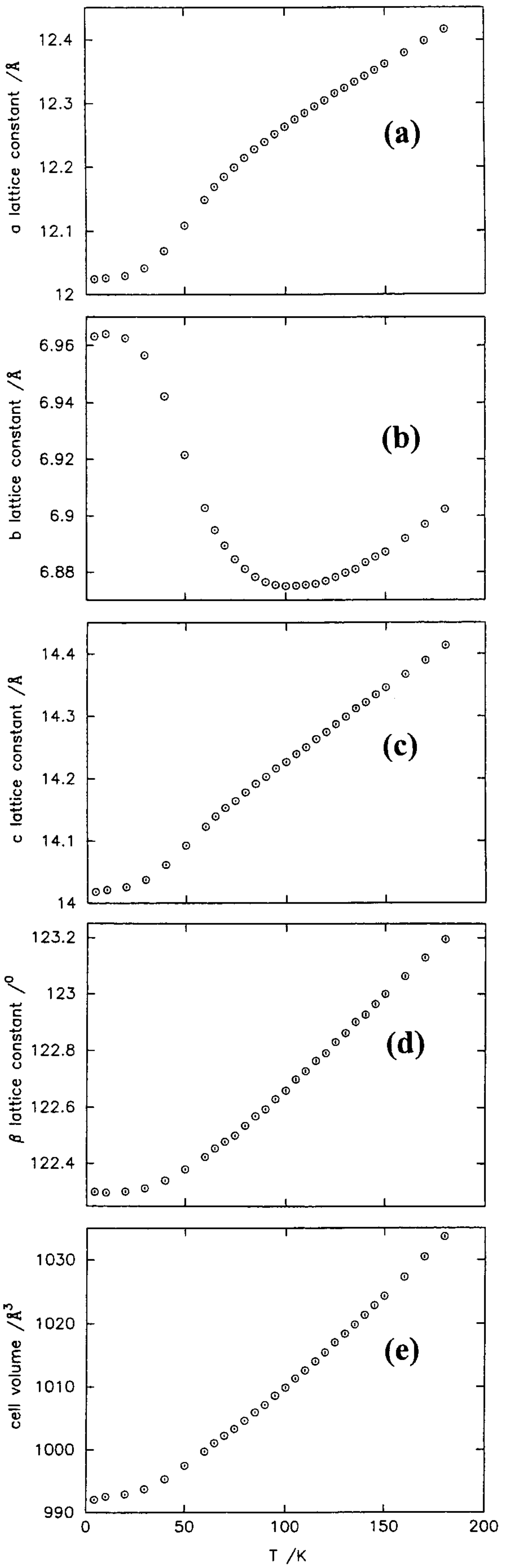

Figure 3. (a−d) Refined lattice constants and (e) unit cell volume of Al_2Me_6-d_{18} at a series of temperatures in the range 10−180 K.

K, before returning to more normal behavior above this temperature.

The *b* unit cell dimension defines the axis along which layers of Al_2Me_6 molecules are stacked. Tetramers are known to form for certain AlR_2H species,[12] and one possible explanation for this unusual behavior invokes a weak dimer−dimer stacking interaction (i.e. $Al_2Me_6\cdots Al_2Me_6$) which disappears at higher temperatures as thermal motion become more significant. However, the Al···Al correlation length is long (ca. 6.9 Å), since this distance essentially mirrors the *b*-axis behavior, although the plane of the dimer is not exactly parallel to the cell *a*−*c* plane. Accordingly, we regard a weak dimer−dimer bonding interaction as an unlikely explanation for the phenomenon.

The layering of the structure along *b* is also manifest in the short D···D intermolecular contacts presented in Table 2. The majority of contacts, and indeed the shortest of these contacts, lie in the *a*−*c* direction. Increasing thermal motion of the molecule with temperature could thus be accommodated by an initial contraction along the more compliant *b* direction. The inelastic neutron scattering spectrum of crystalline Al_2Me_6-d_{18} shows a manifold of features in the region 80−110 cm^{-1}, corresponding to CD_3 torsional motions.[20] These vibrations will become significantly populated over the temperature range characterized by the contraction in *b*. Around 105 K the intermolecular contacts are more isotropic, and positive thermal expansion is observed for all cell axes. Accordingly, we regard this increasing thermal motion to be the most likely explanation for the unusual behavior observed for *b*. Unfortunately, a detailed study of the structural evolution with temperature has not been possible from the limited variable-temperature data available from the current study. We are aware in addition of reports of single crystals shattering below ca. 125 K;[21] hence, a structural phase transition at or around this temperature cannot be ruled out. The variation of cell parameters with temperature suggests that such a phase transition would be non-first-order.

Conclusions

The molecular structure of Al_2Me_6 has been determined by powder neutron diffraction studies of a perdeuterated sample at 4.5 K, and the long-standing question regarding the nature and the geometry of the bridge bonding has been settled. Variable-temperature studies of the supramolecular structure in the crystal show unusual behavior along the Al_2Me_6 stacking axis: this is considered most likely to arise from thermal motion of the methyl groups as the temperature is raised.

Supporting Information Available: Listings of unit cell data, refined structural coordinates, and atomic displacement parameters for Al_2Me_6-d_{18} at 4.5 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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